INVESTIGATION OF THE THERMAL DECOMPOSITION OF ACETALDEHYDE

By

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The pyrolysis of acetaldehyde has been investigated at temperatures between 495 and 540 °C and at initial pressures of 25—200 torr. The reaction was followed by pressure measurements and by G.C. analysis. 3/2 order rate constants were calculated from the measured rate of formation of major products and from pressure measurement data. Arrhenius parameters are given for the overall decomposition and for the initiation step. Among the minor products, the rates of formation of hydrogen, ethane, ethylene, and acetone were measured. The routes of their formation are discussed and a simple mechanism for the decomposition of acetaldehyde is proposed.

Introduction

Among the thermal decomposition reactions, one of the most investigated model compounds is the acetaldehyde. According to STEACIE [1] this intense and permanent interest may be explained by the circumstance that "The acetaldehyde decomposition is remarkable for the lack of agreement of both mechanism and the experimental fact, and the complications involved". This statement is valid even after two decades. In consequence of this fact, a few years ago we have started to investigate the thermal decomposition of acetaldehyde and the same circumstances offer reasons to summarize the main data on the kinetics and mechanism of the decomposition.

The primary aim of our investigation was to study the overall kinetics of reaction to give some data in connection with the formation of minor products and to establish the route of their formation during the decomposition.

The acetaldehyde decomposes at 450—600°C and at medium pressures (30—300 torr) with a well measurable rate; the major products of decomposition are CO and CH_4, which form in equal amount. Besides the main products, hydrogen, acetone, ethylene, and propionaldehyde form in small amounts. The stoichiometric equation of decomposition is

$$CH_3CHO \rightarrow CH_4 + CO.$$

During the decomposition the change in mole number is 2, so the reaction can easily be followed manometrically. The relationship between the changes in mole number and pressure is verified by different authors [2, 20]. In seasoned vessel the decomposition is homogeneous, but in some percent heterogeneous reactions were observed, too [3, 5, 10].

At very low pressures the kinetics of decomposition and the composition of products change significantly. According to COLLIN and DELPLACE [6], at pressures of 0.1 torr the main products of the decomposition are acetylene, ethylene and water.

Though the stoichiometry of decomposition is simple and homogeneous, however, regarding the problem of reaction mechanism, contradictionary opinions were formed and are found in different reviews [7—9].

Order of the reaction

According to KASSEL's opinion [11] the reaction is 3/2 in order and the mechanism of the decomposition is complex. LETORT [12, 24], on the basis of very detailed investigations, distinguished two orders of the reaction, one as function of initial rates (n_0) and one as a function of conversion. The value of $n_0 = 1.5$, while n changes between 1.65—2.3. The existence of these two orders is due to the inhibiting effect of reaction products. The n_0 value, calculated on the basis of initial rates is proved by several authors [3, 13, 15—19].

The Arrhenius parameters determined from the temperature dependence of the 3/2 order rate constants in the temperature range 429—521°C are the following [20]:

$$k_0 = 4 \cdot 10^{12} \exp(-48.00/RT)\ 1^{1/2}\ \text{mole}^{-1/2}\ \text{min}^{-1}.$$

Reaction mechanism

The first mechanism of the decomposition was described by RICE and HERZFELD [21] in 1934.

$$CH_3CHO \rightarrow CH_3 + CHO \quad (1)$$

$$CHO \rightarrow CO + H \quad (2)$$

$$H + CH_3CHO \rightarrow H_2 + CH_3CO \quad (3)$$

$$CH_3CO \rightarrow CH_3 + CO \quad (4)$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \quad (5)$$

$$2\,CH_3 \rightarrow C_2H_6 \quad (6)$$

$$CH_3 + CH_3CO \rightarrow CH_3COCH_3 \quad (7)$$

$$2\,CH_3CO \rightarrow (CH_3CO)_2 \quad (8)$$

Among the three termination steps, the most important was considered to be (6), the ethane-producing reaction, and it was possible to interpret the experimentally observed 3/2 order of reaction.

On the basis of new experimental results, this mechanism has to be revised and extended. According to the original RICE—HERZFELD mechanism, besides the major products only ethane and hydrogen formation take place. At 500 °C a lot of other products were detected by several authors [17, 18, 22]. On the basis

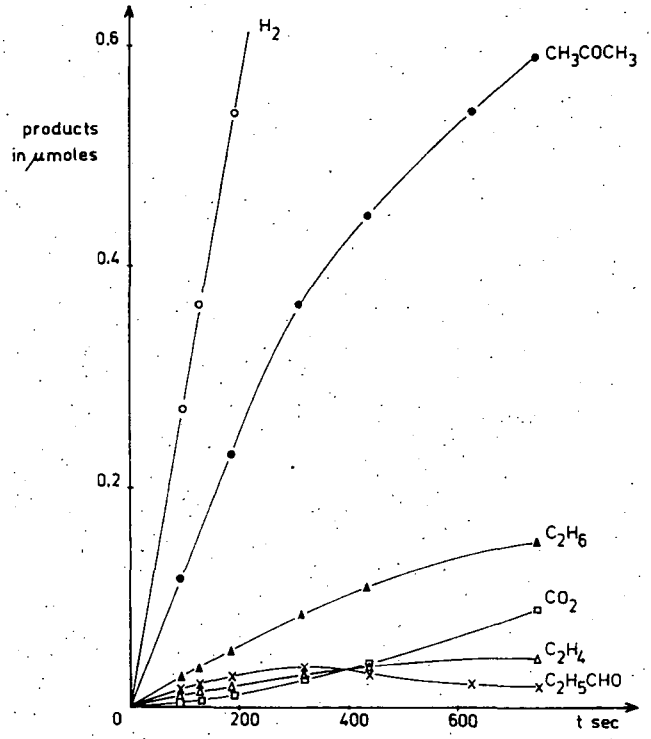

Fig. 1. Products of pyrolysis at 523°C, $p_{ald} = 117$ torr

of the original RICE—HERZFELD mechanism, the existence of this products cannot be explained.

In Fig. 1 we have shown a product distribution curve, using the analytical data of LAIDLER and LIU. In the curve the major products are not plotted.

Table I

The products of acetaldehyde pyrolysis according to literature

Major products	Minor products	Products in trace amounts	Compounds which were not obtained during pyrolysis (according to [22])
	H_2	CH_2CO[18]	HCHO
	CH_3COCH_3	C_3H_6[4, 6, 22, 28]	CH_2CO
	C_2H_6	H_2O[6, 28]	$CH_3OCH{=}CH_2$
CO	C_2H_4[4, 13, 17, 18, 22, 23]	C_2H_2[6]	$(CH_3CO)_2$
CH_4	C_2H_5CHO[17, 18, 22]	C_2H_5OH[17]	CH_3OH
	CO_2[4, 17, 18, 22, 23]	$CH_3CH{=}CHCHO$[22]	C_2H_5OH
		$CH_3COOC_2H_3$[22]	$(CH_3)_2CHOH$
			H_2O

In Table I we collected the products which were detected by several authors during the pyrolysis of acetaldehyde. In the first column of Table I the major products are shown, in the second the minor products, in the third the products formed in trace amounts (which are not always detectable). The fourth column lists the compounds (according to SCHUCHMAN and LAIDLER [22]), which could be formed, but have not been detected so far among the products of pyrolysis.

The problem of formation of minor products

H_2. According to the original Rice—Herzfeld scheme the rate of formation of hydrogen is the measure of the rate of the initiation step. However, detailed investigations did not confirm this fact. TRENWITH [5] observed an induction period for hydrogen production at 502—536 °C and in the pressure range 100—300 torr, where the order of hydrogen production was found to be 2. Investigations with specially purified acetaldehyde [18, 19, 23] did not confirm these results, no induction period was found and the order of hydrogen formation was 1.4 and 1.35. It is presumable, that the induction period observed by TRENWITH is due to the contaminations of acetaldehyde. To explain the experimental results, other hydrogen producing steps have to be supposed.

Acetone. It is an easily detectable product during the pyrolysis, its formation is described in the Rice—Herzfeld scheme, with the combination of methyl and acetyl radicals. According to the analytical measurements, the amount of acetone formed during the pyrolysis is several times higher than that of the ethane. On the basis of this fact, DEXTER and TRENWITH [17] assumed that the main termination step is the methyl+acetyl radical reaction. This assumption can easily confuted. At 500 °C the acetyl radical is thermally unstable and quite easily decomposes, therefore, its concentration is low in the system (biacetyl could not be detected during the pyrolysis). If the assumption of DEXTER—TRENWITH is accepted, then the 3/2 order is valid only in the case when the initiation step is of second order. This contradicts the experimental facts, because the order of the initiation step is close to 1. According to EUSUF and LAIDLER [16] the acetone is formed in the

$$CH_3+CH_3CHO \rightarrow CH_3COCH_3+H$$

reaction. The order of acetone production is 3/2.

Ethane. Easily detectable termination product of decomposition. The order of its production (using carefully purified acetaldehyde) at higher pressures is about 1 (1.1 [18], 1.2 [23]) and below 80 torr a significant fall off was observed, which points to the pressure dependence of the termination step.

Propionaldehyde. WALL and MOORE [35] suggested it to be a termination product during the copyrolysis of acetaldehyde and acetaldehyde-d_4. Its formation was described by the following steps:

$$CH_3+CH_3CHO \rightarrow CH_4+CH_2CHO$$

$$CH_2CHO+CH_3 \rightarrow CH_3CH_2CHO.$$

The propionaldehyde was detected first by TRENWITH [5] and its existence was confirmed by other authors [18, 22], too.

Other minor products. A number of authors have detected ethylene and CO_2 [4, 13, 17, 18, 22, 23]. There are some differences in the interpretation of the experimental data in the literature. TRENWITH assumes ethylene as a primary product of the decomposition and for its formation he considers the decomposition of CH_2CHO radical and the dimerization of CH_2 biradical into ethylene. (This assumption can hardly be accepted). LIU and LAIDLER measured a much lower rate of ethylene production, but they confirmed that ethylene is a primary product. The order of its formation at 540 °C is 1.5 and its formation can be described by the following steps:

$$CH_3+CH_3CHO \rightleftharpoons CH_3—O—CH—CH_3$$

$$CH_3—O—CH—CH_3 \rightarrow CH_3O+C_2H_4.$$

In a recent paper, LAIDLER and SCHUCHMAN [22] suggested the following steps for the ethylene formation

$$H+CH_2=CHOH \rightleftharpoons CH_2CH_2OH \rightarrow C_2H_4+OH.$$

In this step they assume the vinyl alcohol form of aldehyde, however this assumption has no experimental evidence.

Similar problems arise in connection with the CO_2 formation. TRENWITH considers the CO_2 to be a secondary product which forms in the

$$2\,CO \rightarrow CO_2+C$$

reaction step.

According to LAIDLER and LIU the CO_2 is a primary product; for its formation they mention several assumptions, for example the oxidation of CO to CO_2, the wall reaction of acetaldehyde to propylene and water. In connection with TRENWITH's assumption, LAIDLER points out that this reaction does not take place around 500 °C.

It can be seen from Table I that there are some other minor products, which were detected during the pyrolysis by several authors. However, this products were formed in a very small (often in trace) amount, their existence was not always confirmed by more recent investigations, the formation of some products (*e.g.* ketene) was even excluded. The existence of minor products and their rate of formation is strongly influenced by the contaminations of the starting aldehyde, as LAIDLER and LIU have pointed out [4]. In order to describe the formation of these products in the mechanism, sometimes very speculative steps have to be used. As an illustration, we have shown the mechanism of acetaldehyde decomposition suggested by SCHUCHMAN and LAIDLER [22] which is an extended Rice—Herzfeld scheme. Applying this mechanism the authors are able to explain the formation of all products detected by them during the pyrolysis. Steps (1)—(6) are those assumed in the Rice—Herzfeld mechanism.

$$H+CH_3CHO \rightarrow H_2+CH_2CHO \tag{7}$$

$$CH_3+CH_3CHO \rightarrow CH_4+CH_2CHO \tag{8}$$

$$CH_2CHO+CH_3CHO \rightleftharpoons CH_3\underset{\displaystyle O—}{\underset{|}{C}}HCH_2CHO \rightarrow CH_3COCH=CHOH+H \tag{9}$$

$$CH_2CHO + CH_3CHO \rightarrow CH_3CHO + CH_3CO \quad (10)$$

$$CH_2CHO + CH_3CHO \rightarrow CH_3\underset{\underset{O-}{|}}{C}HOCH=CH_2 \rightarrow CH_3COOCH=CH_2 + H \quad (11)$$

$$CH_3 + CH_3CHO \rightarrow CH_3COCH_3 + H \quad (12)$$

$$H + CH_2=CHOH \rightleftharpoons CH_2CH_2OH \rightarrow C_2H_4 + OH \quad (13)$$

$$CH_3 + CH_2=CHOH \rightleftharpoons CH_2CH(CH_3)OH \rightarrow C_3H_6 + OH \quad (14)$$

$$OH + CH_3CHO \rightarrow H_2O + CH_3CO \quad (15)$$

$$CH_3 + CH_2CHO \rightarrow C_2H_5CHO \quad (16)$$

$$CH_3CHO + CH_3CHO \xrightarrow{wall} C_3H_6 + CO + H_2O \quad (17)$$

$$CH_3CHO + CH_3CHO \xrightarrow{wall} C_3H_6 + CO_2 + H_2 \quad (18)$$

$$CH_3CHO + CH_3CHO \xrightarrow{wall} CH_3CH=CHCHO + H_2O \quad (19)$$

Experimental

The decomposition was carried out in a conventional static system. The cylindrical Supremax reaction vessel of 250 cc capacity was enclosed in an electrically heated furnace. The temperature of the vessel was controlled within ± 0.5 °C. The reaction was followed by pressure measurements and by G.C. analysis. The apparatus used and the procedure was described in detail previously [27].

After decomposition, the reaction mixture was led into a series of traps at the temperature of liquid air, the non-considerable fraction was then collected and measured by a Toepler gauge. The G.C. analysis was carried out using a Carlo Erba Fractovap Model C ATC/f apparatus, equipped with a hot wire detector. The non-condensables were analyzed on a 2.5 m, 60—80 mesh silicagel column ($\varnothing = 0.5$ cm) maintained at 50 °C. For the condensables we used 1.6 m long column of 20% β,β'-oxydipropionitrile on Chromosorb P, silanized (60—80 mesh) at 50 °C. Hydrogen was used as carrier gas in both cases at a flow rate of 60 ml/min. The hydrogen was analyzed on a 2.5 m Molecular Sieve 5A column (60—80 mesh) maintained at 50 °C, using nitrogen as carrier gas (60 ml/min). The analysis of minor products (*e.g.* C_2H_6, C_2H_4, etc.) was done on a chromatograph Carlo Erba Fractovap Mod. C type AID/f, equipped with FID, using 2.5 m silicagel column (60—80 mesh) at 80 °C, using nitrogen as carrier gas ($v = 30$ ml/min). In some runs, we made mass spectrometrical analysis, using a Finnigan mass spectrometer type 1016 S/L (quadrupole system). The energy of ion source was 70 eV, m/e range 1—100.

Materials. Acetaldehyde, obtained from Fluka, was purified by a number of bulb to bulb distillations at -78 °C, in vacuo. The middle fraction was collected and stored in the absence of air and light at room temperature. No trace impurity was revealed by G.C. Methane, hydrogen and nitrogen (high purity) were taken from cylinders and, after the usual purification processes, were led into the storing vessels. The carbon monoxyde was prepared by dropping sulfuric acid on sodium formate, dried by passing through traps at -180 °C.

Results

According to our measurements, the acetaldehyde starts to decompose in a measurable extent at 460 °C; above 550 °C the decomposition will be extremely fast. Therefore, we carried out our experiments at 495.5, 512, 527.5 and 539.5 °C at initial pressures of 25, 50, 80, 100, 150 torr and at different conversions (5—70%). During the reaction, we measured the pressure increase and at the end of the reaction we determined the amount of major products (CO, CH_4), the unreacted aldehyde, and some of the minor products (H_2, C_2H_6, CH_3COCH_3, etc.) by G.C.

The kinetics of formation of major products. Some typical concentration—time plots for CO and CH_4 formation are shown in Fig. 2. The shape of the curves agrees

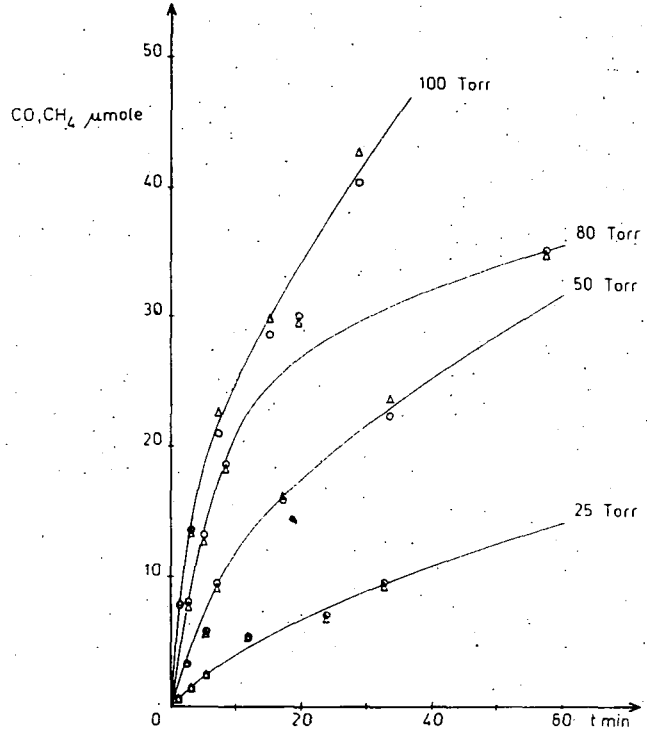

Fig 2. Major products *vs.* time curves at 527.5 °C, ○ CH_4; △ CO

well in the case of CO and CH_4 and the amounts of major products are equal during the reaction, as it can be seen from Fig. 2. The shape of the curves remains similar if the pressure increase is plotted as a function of time. It can be established, from the plots that there is no induction period in the formation of major products and their rate of formation is proportional to the initial concentration of acetaldehyde. Due to the equal amount of major products during the pyrolysis, further we used only one data.

Mass Balance. Making a mass balance for the major products and the starting material, we may establish that, from the decomposing aldehyde, CH_4 and CO form in a proportional amount, as it can be seen in Fig. 3, where the results of a series of experiments ($p_0 = 100$ torr and $t = 527.5$ °C) are shown. This mass balance is not disturbed by the minor products, because their concentrations are not comparable with those of the major products.

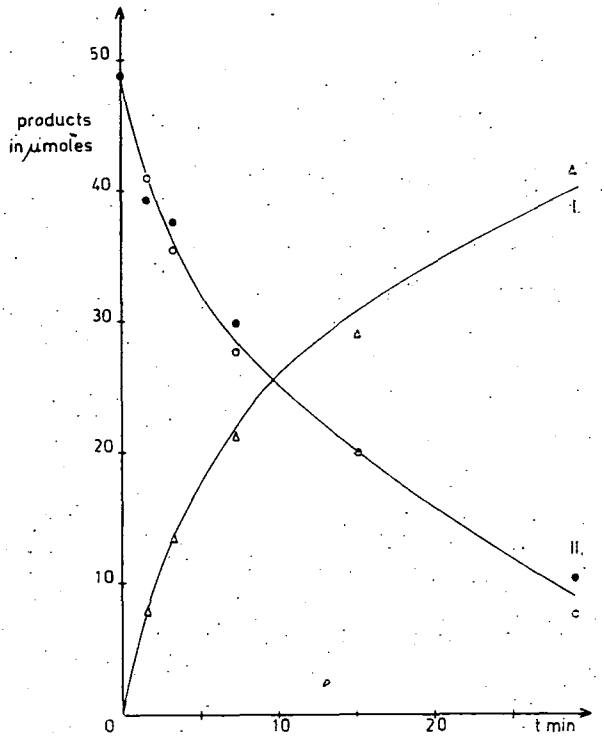

Fig. 3. Mass balance curve at 527.5 °C, $p_{ald.} = 100$ torr

In Fig. 3, curve I shows the pressure increase, while △ symbols denote the analytically determined CH_4 amounts. The two curves fit well and this fact means that the pressure increase is proportional to the amounts of major products formed. This fact also gives the possibility to use the pressure—time data in some cases to elucidate the kinetics of this decomposition. On curve II the decrease of the concentration of acetaldehyde (○ determined analytically, ● determined manometrically) is plotted. The agreement of both curves shows the fitting of the analytical data obtained from two different sources.

Determination of the overall order of reaction. With the aid of the initial rates (w_0), determined from the product—time curves the overall order (n_0) was determined. From the same experiments, the overall order n can be calculated as a function of CH_4 formed. These orders were calculated from our data obtained from both

Table II

The overall order of reaction as a function of time and temperature

t °C	Analytical data						Pressure measurement data					
	at the formation of						at the formation of					
	n / n_0	1	2	4	7	10	n / n_0	1	2	4	7	10
		μmole CH_4						μmole CH_4				
495.5	1.43 ±0.16	1.40	1.42	1.37	1.38	1.40	–	—	—	—	—	—
512	1.57 ±0.23	1.52	1.48	1.38	1.33	1.39	1.49 ±0.02	1.54	1.55	1.57	1.56	1.65
527.5	1.57 ±0.15	1.56	1.55	1.52	1.46	1.33	1.49 ±0.02	1.50	1.52	1.53	1.56	1.62
539.5	1.64 ±0.13	1.64	1.60	1.53	1.39	1.30	1.53 ±0.02	1.56	1.60	1.65	1.74	—
550.5	—	—	—	—	—	–	1.54 ±0.02	1.57	1.63	1.67	1.72	1.44
Mean value:	1.55						1.51					

pressure—time measurements as well as analytically, and the results are listed in Table II.

In both cases the initial rates are derived from curve-fitting data obtained by computer and the error limits are given by standard deviations, calculated with linear least square methods. It can be seen from Table II that the n_0 values increase slightly with increasing temperature (this increase is smaller in the case of pressure—time data). The mean value of n_0 data, calculated from pressure measurements is very close to 1.5 and is in excellent agreement with the data given in the literature. However, the analytically determined n_0 values show a significant deviation from 1.5. This is probably due to errors in analytical determination.

As it can be seen from Table II — in contrary with LETORT's results — big increase of order with time could not be observed in our experiments and the value of n never exceeds 1.8.

Determination of Arrhenius parameters. The $n_0=3/2$ order is demonstrable with the following simple method. As known, the rate constant for 3/2 order reactions is described by the following equation:

$$k = \frac{2}{t}(c^{-1/2} - c_0^{-1/2})$$

where c_0=initial concentration, c=concentration at time t. Introducing the symbols $c/c_0=x$ and $c_0^{1/2}t=\tau$, the result will be

$$x^{-1/2} = 1 + \frac{1}{2}k\tau .$$

Table III

3/2 *Order overall rate constants,* $k \cdot 10^{-2}$ *(in* $l^{1/2}$ $mole^{-1/2}$ sec^{-1}*), calculated from the analytical results at different temperatures and initial aldehyde pressures*

p_{ald} → / t °C	25	50	80	100	150 torr	Mean value
495.5	5.61 ±2.12	3.89 ±0.94	4.55 ±0.47	4.17 ±0.35	3.73 ±0.49	4.39±0.84
512	—	6.74 ±0.73	7.76 ±0.69	6.84 ±0.52	7.29 ±1.31	7.16±0.81
527.5	12.30 ±1.64	12.68 ±0.85	14.56 ±0.92	12.86 ±0.80	14.01 ±0.70	13.23±0.98
539.5	17.89 ±0.72	21.37 ±1.86	25.05 ±1.39	—	21.18 ±1.39	21.37±1.35

If the 3/2 order is valid for the decomposition, then plotting $x^{-1/2}$ *vs.* τ, we obtain a straight line of slope $k/2$ and the intercept will be 1. In Fig. 4 the results of a series of typical experiments at 512 °C, calculated from the methane analysis data can be seen. The initial pressure of aldehyde changed between 50—150 torrs. Within the limits of experimental error a straight line was obtained. Using this method we calculated the overall rate constants from the analytical data (by means of least square methods) as it can be seen in Table III.

From the temperature dependence of these rate constants (see Fig. 5) we calculated $E_a = 47.09 \pm 1.32$ kcal/mole for the activation energy of the decomposition,

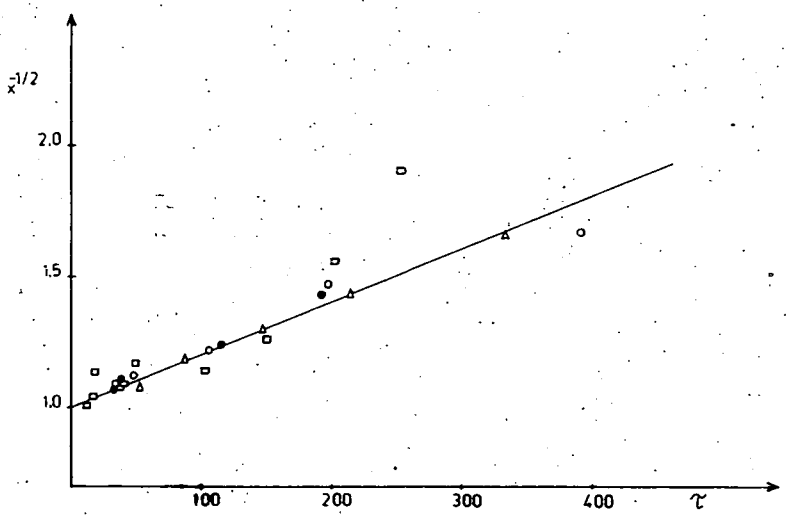

Fig. 4. Relation between $1/x^{1/2}$ and $c_0^{1/2}t$ at 512 °C. The data are calculated on the basis of methane analysis. $p_{ald.}$ = □ 50 torr; ○ 80 torr; △ 100 torr; ● 150 torr

Table IV

3/2 *Order overall rate constants,* $k \cdot 10^{-2}$ *(in* $l^{1/2}$ mole$^{-1/2}$ sec^{-1}*), calculated from pressure-time measurements, at different temperatures and initial aldehyde pressures*

p_{ald} / t °C	50	100	200 torr
495.5	—	—	0.99±0.06
512	2.10±0.07	2.20±0.03	1.91±0.05
527.5	3.80±0.04	3.96±0.05	4.07±0.04
539.5	6.34±0.05	6.30±0.04	—
544.8	7.13±0.09	7.39±0.04	7.41±0.05
550.5	9.49	—	—
561.5	12.94±0.12	13.47±0.05	—

and $A = 5.36 \pm 2.13 \cdot 10^{12}$, for the A value which agree satisfactorily with earlier data. The overall rate constants may be given by

$$k = 5.36 \cdot 10^{12} \exp(-47.09/RT)\ l^{1/2}\ \text{mole}^{-1/2}\ \text{sec}^{-1}$$

in the temperature range 495—550 °C.

Table IV contains the mean values of overall rate constants, calculated from pressure measurements with the aid of the following expression:

$$k = \frac{2}{t}(c^{-1/2} - c_0^{-1/2})$$

From these data, we obtained the Arrhenius parameters $E_a = 49.52 \pm 1.26$ kcal/mole,

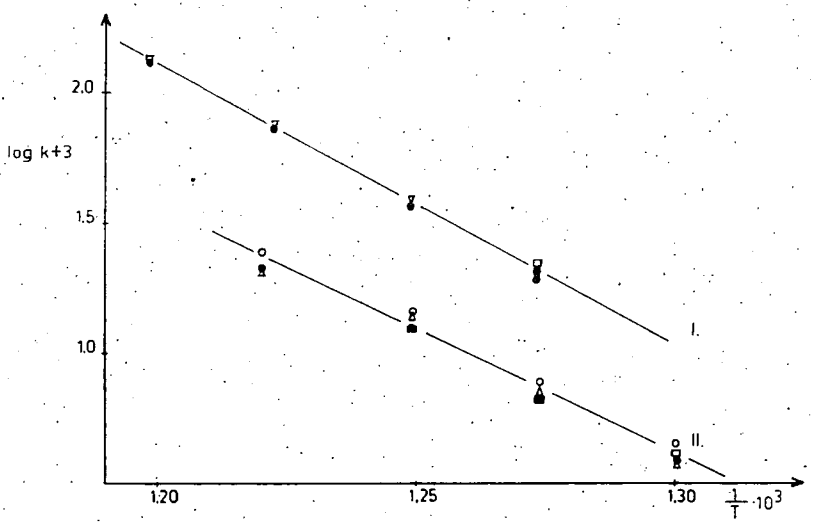

Fig. 5. Arrhenius plot of the 3/2 order overall rate constants. Initial aldehyde pressures: ● 50 torr; ○ 80 torr; □ 100 torr; △ 150 torr; ▽ 200 torr. Curve I is calculated from pressure—time measurements; Curve II from analytical measurements

$A = 2.36 \pm 1.77 \cdot 10^{12}$, and the overall rate constant is

$$k = 2.36 \cdot 10^{12} \exp(-49.52/RT)\ l^{1/2}\ \text{mole}^{-1/2}\ \text{sec}^{-1}$$

The agreement of E_a and A values, calculated from analytical and pressure measurements is quite satisfactory.

Measurement of minor products

H_2. Among the minor products, hydrogen forms in the greatest amount. A typical H_2 yield-time curve is shown in Fig. 6. As it can be seen from Fig. 6, the curves are similar to the yield—time curves of major products and there is no sign of induction period, in contrary with TRENWITH [5]. The order of hydrogen production was determined from the initial slopes of these curves. The order is 1.36, which agrees well with the value 1.4, determined by LAIDLER [4] and COME [23, 29]. This shows that the simple Rice—Herzfeld mechanism is not valid for the decomposition, because in this case the rate of formation of hydrogen would be a measure of the rate of the initiation step.

Acetone. The product quite easily detectable with hot-wire detector if the initial aldehyde concentration is above 80 torr. The amount of acetone was always

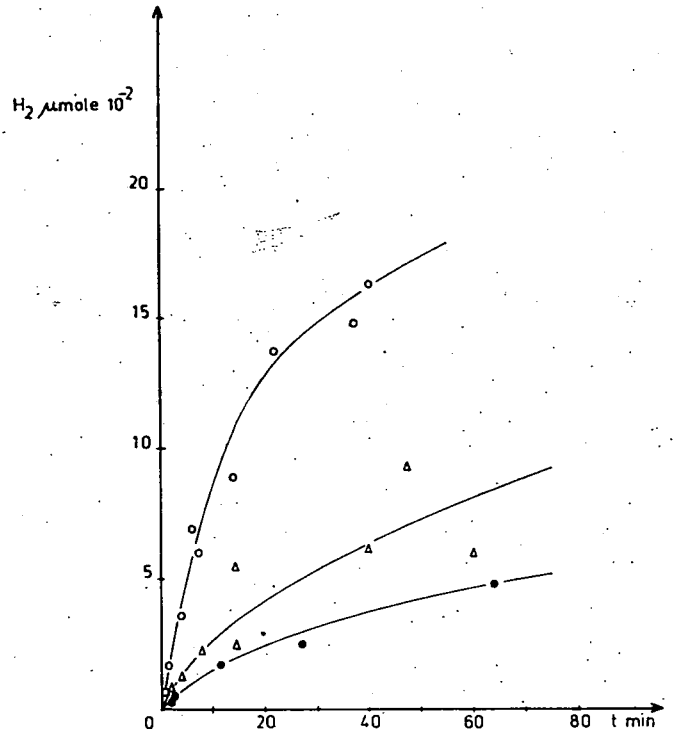

Fig. 6. Typical yield *vs.* time plot for hydrogen formation at 527.5 °C. $p_{ald.}$ = ● 25 torr; △ 50 torr; ○ 100 torr

less than the amount of hydrogen. The shapes of yield—time curves were similar to the curves of major products and no induction period existed in this case either.

Ethane. One of the termination products of decomposition. It was produced in smaller amounts than the former ones. No induction period was observable and the yield curves of ethane production as a function of conversion and concentration showed a similar shape as those of major products.

Ethylene. The amount of this product is comparable with, though smaller than that of ethane. The characteristics of the yield—time curves are the same as in the case of ethane.

Propionaldehyde. According to the literature mentioned earlier, this compound is the other termination product besides ethane. During our investigations it could be detected only in a trace amount by mass spectroscopy, therefore we did not make detailed experiments concerning its formation.

Carbon dioxide. It could be detected in trace amount only; no quantitative measurements were made.

Other products. During the analysis of decomposition products we could not find propylene, ethanol, higher aldehydes [22] and water. These informations were very useful for suggesting the mechanism given below.

In Fig. 7 we present the analytical data obtained by the decomposition of 80 torr acetaldehyde at 482 °C. The ratio of the products is easily comparable in the figure.

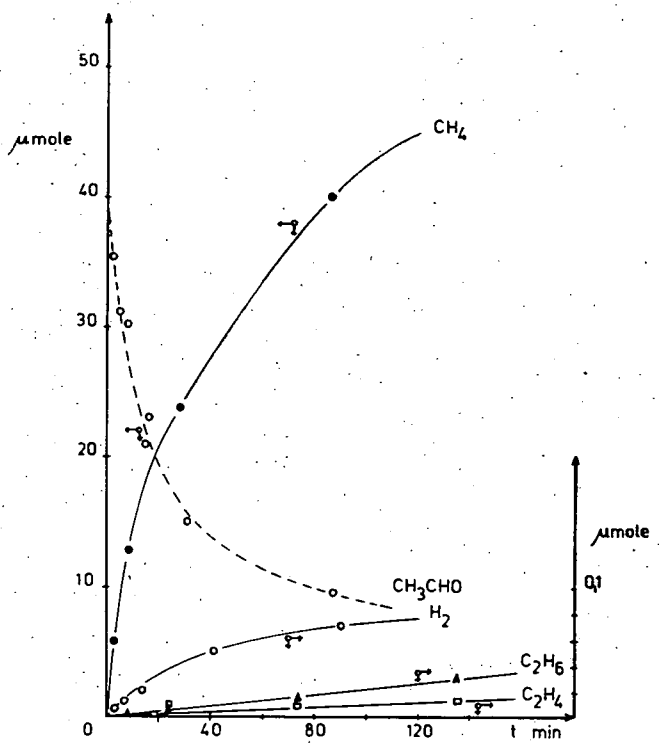

Fig. 7. Products of pyrolysis at 482 °C. $p_{ald.} = 80$ torr

Discussion

As mentioned in the introduction, the simple Rice—Herzfeld scheme is not suitable for describing the mechanism of the thermal decomposition of acetaldehyde, especially the production of minor products. On the basis of the literature and our experimental data we suggest the following mechanism, which is an extended Rice—Herzfeld scheme.

The initiation step is the unimolecular decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_3 + CHO \qquad (1)$$

In the pressure range used in our experiments the reaction is in its first order region. This step is followed by the chain propagation step

$$CHO \rightarrow CO + H. \qquad (2)$$

The H atoms react with the aldehyde molecule

$$H + CH_3CHO \rightarrow H_2 + CH_3CO \qquad (3)$$

and

$$H + CH_3CHO \rightarrow H_2 + CH_2CHO. \qquad (7)$$

In consequence of the higher reactivity of formyl hydrogen, step (3) occurs more frequently than step (7) requiring a higher activation energy: $[D(H—CH_2CHO)] \sim \sim 102$ kcal/mole, while $[D(CH_3CO—H)] \sim 87$ kcal/mole [34]. The reaction steps proposed by LAMBERT *et. al.* [37]

$$H + CH_3CHO \rightarrow CH_4 + CHO$$

and

$$CHO + CH_3CHO \rightarrow CO + H_2 + CH_2CHO$$

have no experimental evidence.

Methyl radicals, forming in the initiation step, have two possibilities to react with the acetaldehyde in a H abstraction reaction,

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad (5)$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_2CHO. \qquad (8)$$

The direct determination of the relationship of these two reactions was carried out first by AUSLOOS and STEACIE [25]. According to these authors, reaction (8) is negligible in comparison with reaction (5). The rate constant of step (5) was determined by BRINTON and VOLMAN [32] and the Arrhenius parameters of reaction (8) were estimated by LAIDLER and LIU [18] and SCHUCHMAN and LAIDLER [22]. The estimation is based on similar abstraction reactions of methyl radicals. At 500 °C the k_8/k_5 ratio $=0.116$ [22], but in the literature published earlier by the same authors the values 10^{-4} [18] and 10^{-2} [4] are found. According to our current investigations, the highest value is the most probable.

The acetyl radical arising from the reaction (5) at about 500 °C decomposes rapidly

$$CH_3CO \rightarrow CH_3 + CO \qquad (4)$$

so further reactions of this radical do not exist. Since we did not detect ketene as

reaction product, the reaction

$$CH_3CHO + H \rightarrow CH_2CO + H_2$$

must be excluded from the mechanism [36]. The fate of CH_2CHO radicals arising from reactions (7) and (8) may be as follows:

1. Decomposition according to the equation

$$CH_2CHO \rightarrow CH_2CO + H.$$

Ketene was not found as reaction product, though it is stable under these experimental conditions (450—525 °C) [22]; thus this step has to be rejected.

2. Reaction with the acetaldehyde molecule

$$CH_2CHO + CH_3CHO \rightarrow CH_3CHO + CH_3CO. \qquad (10)$$

The estimated value of k_7 according to LAIDLER is $10^{7.4}$ cc · mole^{-1} · sec^{-1}, the concentration of CH_2CHO radicals $\approx 10^{11.6}$ mole · cc^{-1}, exceeds the concentration of methyl radicals in the system, therefore this radical is of great importance in the mechanism of decomposition. According to BENSON [33], the reactivity of CH_2CHO radicals is similar to that of methyl radicals (in contrary LAIDLER assumes the reactivity to be similar to that of allyl radicals) and its concentration is lower than estimated by LAIDLER.

3. Isomerization to acetyl radicals

$$CH_2CHO \rightarrow CH_3CO.$$

The activation energy of this step is about 47 kcal/mole, which is negligible compared with reaction (7); the estimated ratio of the two reactions is $v_i/v_7 \sim 10^{-2}$.

4. The most probable reaction is the propionaldehyde production, which can be expressed by the following equation

$$CH_3 + CH_2CHO \rightarrow CH_3CH_2CHO. \qquad (16)$$

The fact that propionaldehyde was detected as a product of pyrolysis verifies the existence of this step as termination step, though it has smaller importance than the methyl recombination step.

The methyl radicals reacting with the starting material in a hydrogen rearrangement reaction

$$CH_3 + CH_3CHO \rightarrow CH_3COCH_3 + H \qquad (12)$$

give acetone.

According to LAIDLER's estimation the ratio of the concentrations of acetyl and methyl radicals is $10^{-2}-10^{-3}$, which shows that the most important termination step is the methyl recombination

$$CH_3 + CH_3 \rightarrow C_2H_6. \qquad (6)$$

The formation of easily detectable ethylene may be explained for instance in the following way (by radical isomerization and decomposition)

$$H + CH_3CHO \rightarrow CH_3CH_2O \rightarrow C_2H_4 + OH. \qquad (7a)$$

CO_2 was detected in trace amount, its formation, according to LAIDLER, is the following:

$$2\,CH_3CHO \xrightarrow{wall} C_3H_6 + CO_2 + H_2. \qquad (17)$$

This step explains at the same time the formation of propylene, which we did not find in our case, though its existence seems to be proved from literature.

On the basis of our experiments and literature data, the thermal decomposition of acetaldehyde may be described by the reaction steps (1)—(17) given above.

Since the rate of formation of major products is three orders higher than that of the other products, the aldehyde decomposition can be well approached by the original Rice—Herzfeld scheme. On the basis of this scheme, the equation of decomposition is the following:

$$-\frac{d[CH_3CHO]}{dt} = 2k_1[CH_3CHO] + k_5\left(\frac{k_1}{k_6}\right)^{1/2}[CH_3CHO]^{3/2}.$$

Assuming the consumption of aldehyde to be negligible in the initiation step, this expression can be simplified as follows:

$$-\frac{d[CH_3CHO]}{dt} = +\frac{d[CH_4]}{dt} = k_5\left(\frac{k_1}{k_6}\right)^{1/2}[CH_3CHO]^{3/2}.$$

The value of k_1 may be calculated from the known k_5 [26] and k_6 [30] values. With the aid of k_1 we can determine the Arrhenius parameters of the initiation step.

In Fig. 8, the $\log k_1 - 1/T$ curves, calculated from analytical and pressure—time measurement data, are shown. From these curves the following value of activation energies for the initiation step are obtained:

$E_1 = 81.49 \pm 3.25$ kcal/mole (from pressure—time data)

$E_1 = 79.69 \pm 1.38$ kcal/mole (from analytical data).

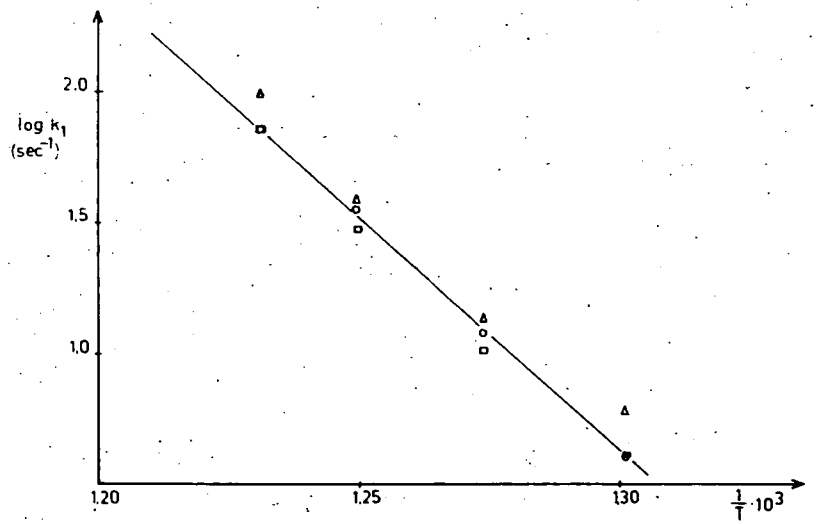

Fig. 8a. Arrhenius plot of the first order rate constants (k_1), calculated from the analytical data. $p_{ald.}$ = □ 50 torr; △ 80 torr; ○ 150 torr

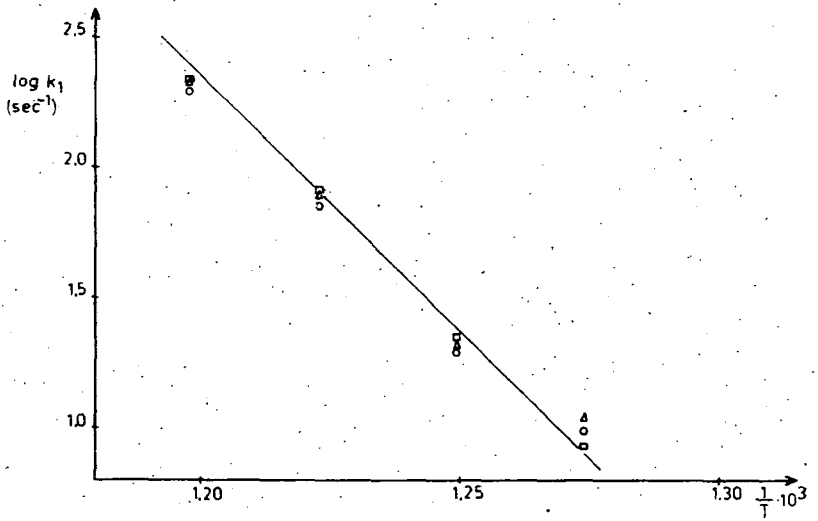

Fig. 8b. Arrhenius plot of the first order rate constants (k_1), calculated from pressure—time measurements. $p_{ald.}$ = ○ 50 torr; △ 100 torr □ 200 torr

while the A values are:

$A_1 = 8.87 \pm 4.42 \cdot 10^{16}$ (from pressure measurement)

$A_1 = 3.88 \pm 2.94 \cdot 10^{16}$ (from analytical data).

These values agree well with the values of other authors, because E_1 varies between 79—82 kcal/mole [23, 4, 14, 31] and $A_1 = 10^{16}$ [23].

The chain length (ν) may be given as the ratio of the overall rate of acetaldehyde decomposition and the rate of chain initiation:

$$\nu = \frac{W_{\text{overall}}}{W_{\text{initiation}}}$$

Table V

Chain lengths as functions of pressure and temperature

p_{ald} / t °C	80	100	200
495.5	—	17000	35950
512	12400	15000	17000
527.5	6200	9300	10700
539.5	4400	—	8600

Using the k_1 value derived from analytical data, the values given in Table V are obtained.

The chain lengths calculated from pressure measurement data are similar.

* * *

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ИЗУЧЕНИЕ ТЕРМИЧЕСКОГО РАСПАДА АЦЕТАЛЬДЕГИДА

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Изучен термический распад ацетальдегида в области температур 495—540 °C при исходных давлениях 25—200 торр. За ходом реакции следили по изменениям давления и газохроматографическим методом анализа. С применением обеих методов были рассчитаны константы скорости, которые независимо от метода, для образования основных продуктов получались соответствующими 3/2 порядку реакции. Для общей реакции и реакции инициирования были определены Аррениусовые параметры. Обсуждены реакции образования побочных продуктов и предложен простой механизм распада ацетальдегида.

TETRAGONALLY DISTORTED TETRAHEDRAL ML_4-COMPLEXES, IV

Splitting of the d^5-Configuration in Strong Ligand Field of D_{2d}-Symmetry

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The energies of spectroscopic terms arising from the splitting, in ligand field of D_{2d}-symmetry, of d^5 strong field configurations have been given in expressions of the electronic repulsion parameters B and C, the three ligand field parameters K, L and M and the distortion angle β.

By using the procedure described in the previous papers [1—3] of this series, energy matrices[1] including the terms of electronic repulsions and electron-ligand interactions of five d-electrons in strong ligand field of D_{2d}-symmetry have been given as follows:

$$^6A_1[a_1b_1b_2e^2]:0 \tag{1}$$

$^4A_1$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$
$[a_1b_1b_2e^2]$	$\frac{35}{3}B+5C$	$\sqrt{\frac{20}{9}}B$	$-\sqrt{\frac{60}{9}}B$
$[a_1b_1b_2e^2]$		$\frac{34}{3}B+5C$	$-\sqrt{\frac{48}{9}}B$
$[a_1b_1b_2e^2]$			$14B+5C$

(2)

$^4A_2$	$[a_1b_1^2e^2]$	$[a_1b_2^2e^2]$	$[a_1b_1b_2e^2]$
$[a_1b_1^2e^2]$	$10B+6C-12L$	C	$\sqrt{18}B$
$[a_1b_2^2e^2]$		$10B+6C+12L$	$\sqrt{18}B$
$[a_1b_1b_2e^2]$			$19B+7C$

(3)

[1] The matrices are symmetrical, thus the indication of the off-diagonal elements above the diagonals is sufficient.

$^2A_1$	$[a_1e^4]$	$[a_1b_1^2b_2^2]$	$[a_1b_1^2e^2]$	$[a_1b_2^2e^2]$	$[a_1^2b_1e^2]$	$[a_1^2b_2e^2]$	$[b_1b_2^2e^2]$	$[b_1^2b_2e^2]$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$
$[a_1e^4]$	$35B+10C-$ $-12K+6M$	0	$\sqrt{2}(3B+C)$	$\sqrt{2}(3B+C)$	$-\sqrt{6}B$	$\sqrt{6}B$	0	0	$3B$	$-\sqrt{27}B$	$\sqrt{72}B$
$[a_1b_1^2b_2^2]$		$35B+10C+$ $+12K-6M$	$\sqrt{2}(3B+C)$	$\sqrt{2}(3B+C)$	0	0	$\sqrt{6}B$	$-\sqrt{6}B$	$3B$	$-\sqrt{27}B$	$\sqrt{72}B$
$[a_1b_1^2e^2]$			$23B+11C-$ $-12L$	C	$-\sqrt{75}B$	0	0	$-\sqrt{75}B$	$\sqrt{\frac{9}{2}}B$	$-\sqrt{\frac{27}{2}}B$	$6B$
$[a_1b_2^2e^2]$				$23B+11C+$ $+12L$	0	$\sqrt{75}B$	$\sqrt{75}B$	0	$\sqrt{\frac{9}{2}}B$	$-\sqrt{\frac{27}{2}}B$	$6B$
$[a_1^2b_1e^2]$					$27B+9C+6K-$ $-6L+4M$	$-3B$	$4B+C$	0	$\sqrt{6}B$	0	$-\sqrt{12}B$
$[a_1^2b^2e^2]$						$27B+9C+6K+$ $+6L+4M$	0	$4B+C$	$\sqrt{\frac{3}{2}}B$	$\sqrt{\frac{9}{2}}B$	$\sqrt{12}B$
$[b_1b_2^2e^2]$							$27B+9C-6K+$ $+6L-4M$	$-3B$	$-\sqrt{6}B$	0	$\sqrt{12}B$
$[b_1^2b_2e^2]$								$27B+9C-6K-$ $-6L-4M$	$-\sqrt{\frac{3}{2}}B$	$-\sqrt{\frac{9}{2}}B$	$-\sqrt{12}B$
$[a_1b_1b_2e^2]$									$\frac{49}{3}B+8C$	$-\sqrt{\frac{100}{3}}B$	$\sqrt{\frac{8}{9}}B$
$[a_1b_1b_2e^2]$										$23B+8C$	$-\sqrt{\frac{8}{3}}B$
$[a_1b_1b_2e^2]$											$\frac{56}{3}B+8C$

(7)

$^2A_2$	$[a_1b_1^2e^2]$	$[a_1b_2^2e^2]$	$[a_1^2b_1e^2]$	$[a_1^2b_2e^2]$	$[b_1b_2^2e^2]$	$[b_1^2b_2e^2]$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$
$[a_1b_1^2e^2]$	$13B+9C-12L$	C	$-3B$	0	0	$-3B$	$-\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{27}{2}}B$
$[a_1b_2^2e^2]$		$13B+9C+12L$	0	$-3B$	$-3B$	0	$-\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{27}{2}}B$
$[a_1^2b_1e^2]$			$27B+9C+6K-6L+4M$	$3B$	$4B+C$	0	0	$-\sqrt{150}B$
$[a_1^2b_2e^2]$				$27B+9C+6K+6L+4M$	0	$4B+C$	$\sqrt{\frac{225}{2}}B$	$-\sqrt{\frac{75}{2}}B$
$[b_1b_2^2e^2]$					$27B+9C-6K+6L-4M$	$3B$	0	$-\sqrt{150}B$
$[b_1^2b_2e^2]$						$27B+9C-6K-6L-4M$	$\sqrt{\frac{225}{2}}B$	$-\sqrt{\frac{75}{2}}B$
$[a_1b_1b_2e^2]$							$25B+10C$	$-\sqrt{12}B$
$[a_1b_1b_2e^2]$								$29B+10C$

(8)

$^2B_1$	$[b_1e^4]$	$[a_1^2b_1b_2^2]$	$[a_1b_1^2e^2]$	$[a_1b_2^2e^2]$	$[a_1^2b_1e^2]$	$[a_1^2b_2e^2]$	$[b_1b_2^2e^2]$	$[b_1^2b_2e^2]$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$
$[b_1e^4]$	$15B+10C-18K-$ $-6L+2M$	0	$-\sqrt{6}B$	0	$\sqrt{2}(B+C)$	0	$\sqrt{2}(3B+C)$	$\sqrt{54}B$	0	$-\sqrt{12}B$
$[a_1^2b_1b_2^2]$		$15B+10C+18K+$ $+6L-2M$	0	$\sqrt{6}B$	$\sqrt{2}(3B+C)$	$-\sqrt{54}B$	$\sqrt{2}(B+C)$	0	0	$-\sqrt{12}B$
$[a_1b_1^2e^2]$			$17B+9C-$ $-12L$	C	$-\sqrt{75}B$	0	0	$-3B$	$\sqrt{\frac{27}{2}}B$	$\sqrt{\frac{9}{2}}B$
$[a_1b_2^2e^2]$				$17B+9C+$ $+12L$	0	$-3B$	$\sqrt{75}B$	0	$-\sqrt{\frac{27}{2}}B$	$-\sqrt{\frac{9}{2}}B$
$[a_1^2b_1e^2]$					$33B+11C+6K-$ $-6L+4M$	$-\sqrt{27}B$	$4B+C$	0	0	$-\sqrt{150}B$
$[a_1^2b_2e^2]$						$27B+9C+6K+$ $+6L+4M$	0	$4B+C$	$\sqrt{\frac{3}{2}}B$	$\sqrt{\frac{9}{2}}B$
$[b_1b_2^2e^2]$							$33B+11C-6K+$ $+6L-4M$	$\sqrt{27}B$	0	$-\sqrt{150}B$
$[b_1^2b_2e^2]$								$27B+9C-6K-$ $-6L-4M$	$-\sqrt{\frac{3}{2}}B$	$-\sqrt{\frac{9}{2}}B$
$[a_1b_1b_2e^2]$									$19B+8C$	$-\sqrt{12}B$
$[a_1b_1b_2e^2]$										$23B+8C$

(9)

$^2B_2$	$[b_2e^3]$	$[a_1^2b_1^2b_2]$	$[a_1b_1^2e^2]$	$[a_1b_2^2e^2]$	$[a_1^2b_1e^2]$	$[a_1^2b_2e^2]$	$[b_1b_2^2e^2]$	$[b_1^2b_2e^2]$	$[a_1b_1b_2e^2]$	$[a_1b_1b_2e^2]$
$[b_2e^3]$	$15B+10C-18K+$ $+6L+2M$	0	0	$\sqrt{6}B$	0	$\sqrt{2}(B+C)$	$-\sqrt{54}B$	$\sqrt{2}(3B+C)$	$3B$	$-\sqrt{3}B$
$[a_1^2b_1^2b_2]$		$15B+10C+18K-$ $-6L-2M$	$-\sqrt{6}B$	0	$\sqrt{54}B$	$\sqrt{2}(3B+C)$	0	$\sqrt{2}(B+C)$	$3B$	$-\sqrt{3}B$
$[a_1b_1^2e^2]$			$17B+9C-$ $-12L$	C	$-3B$	0	0	$-\sqrt{75}B$	$-\sqrt{\frac{27}{2}}B$	$-\sqrt{\frac{9}{2}}B$
$[a_1b_2^2e^2]$				$17B+9C+$ $+12L$	0	$\sqrt{75}B$	$-3B$	0	$\sqrt{\frac{27}{2}}B$	$\sqrt{\frac{9}{2}}B$
$[a_1^2b_1e^2]$					$27B+9C+6K-$ $-6L+4M$	$\sqrt{27}B$	$4B+C$	0	$\sqrt{6}B$	0
$[a_1^2b_2e^2]$						$33B+11C+6K+$ $+6L+4M$	0	$4B+C$	$\sqrt{\frac{225}{2}}B$	$-\sqrt{\frac{75}{2}}B$
$[b_1b_2^2e^2]$							$27B+9C-6K+$ $+6L-4M$	$-\sqrt{27}B$	$-\sqrt{6}B$	0
$[b_1^2b_2e^2]$								$33B+11C-6K-$ $-6L-4M$	$\sqrt{\frac{225}{2}}B$	$-\sqrt{\frac{75}{2}}B$
$[a_1b_1b_2e^2]$									$19B+8C$	$-\sqrt{12}B$
$[a_1b_1b_2e^2]$										$23B+8C$

(10)

${}^4E$	$[a_1^3e^3]$	$[b_1^3e^3]$	$[b_2^3e^3]$	$[a_1b_1e^3]$	$[a_1b_1e^3]$	$[a_1b_2e^3]$	$[a_1b_2e^3]$	$[b_1b_2e^3]$	$[b_1b_2e^3]$ ...
$[a_1^3e^3]$	$45B+10C+$ $+7M$	$4B+C$	$4B+C$	$-\sqrt{\frac{75}{2}}B$	$-\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{75}{2}}B$	$-\sqrt{\frac{9}{2}}B$	0	0
$[b_1^3e^3]$		$15B+10C-12K-$ $-12L-M$	C	$-\sqrt{\frac{75}{2}}B$	$\sqrt{\frac{9}{2}}B$	0	0	$-\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{27}{2}}B$
$[b_2^3e^3]$			$15B+10C-12K+$ $+12L-M$	0	0	$\sqrt{\frac{75}{2}}B$	$\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{9}{2}}B$	$\sqrt{\frac{27}{2}}B$
$[a_1b_1e^3]$				$26B+9C-6K-$ $-6L+3M$	$\sqrt{3}B$	$-\frac{3}{2}B$	$\sqrt{\frac{27}{4}}B$	$\sqrt{\frac{75}{4}}B$	$-\frac{3}{2}B$
$[a_1b_1e^3]$					$22B+9C-6K-$ $-6L+3M$	$-\sqrt{\frac{9}{2}}B$	$\frac{9}{2}B$	$\frac{3}{2}B$	$\sqrt{\frac{147}{4}}B$ (11a)
$[a_1b_2e^3]$						$26B+9C-6K+$ $+6L+3M$	$-\sqrt{3}B$	$\sqrt{\frac{75}{4}}B$	$\frac{3}{2}B$
$[a_1b_2e^3]$							$22B+9C-6K+$ $+6L+3M$	$-\frac{3}{2}B$	$\sqrt{\frac{147}{4}}B$
$[b_1b_2e^3]$								$15B+9C-$ $-12K-M$	0
$[b_1b_2e^3]$ ...									$21B+9C-$ $-12K-M$

(11b) (cont.)

^3E	... $[a_1^2b_1^2e]$	$[a_1^2b_2^2e]$	$[b_1^2b_2^2e]$	$[a_1b_1b_2^2e]$	$[a_1b_1b_2^2e]$	$[a_1b_1^2b_2e]$	$[a_1b_1^2b_2e]$	$[a_1^2b_1b_2e]$	$[a_1^2b_1b_2e]$
$[a_1^2e^3]$	$3B+C$	$3B+C$	0	0	0	0	0	$-\sqrt{\frac{81}{2}}B$	$-\sqrt{\frac{27}{2}}B$
$[b_1^2e^3]$	$B+C$	0	$3B+C$	0	0	$\sqrt{\frac{3}{2}}B$	$-\sqrt{\frac{9}{2}}B$	0	0
$[b_2^2e^3]$	0	$B+C$	$3B+C$	$\sqrt{6}B$	0	0	0	0	0
$[a_1b_1e^3]$	$-\sqrt{6}B$	0	0	$3B+C$	0	$\frac{9}{2}B$	$\sqrt{\frac{27}{4}}B$	$-\sqrt{\frac{3}{4}}B$	$\frac{3}{2}B$
$[a_1b_1e^3]$	0	0	0	0	$3B+C$	$\sqrt{\frac{243}{4}}B$	$-\frac{3}{2}B$	$\frac{3}{2}B$	$\sqrt{\frac{3}{4}}B$
$[a_1b_2e^3]$	0	$\sqrt{6}B$	0	0	$-\sqrt{27}B$	$-\frac{1}{2}(3B+C)$	$\sqrt{\frac{3}{4}}(3B+C)$	$-\sqrt{\frac{3}{4}}B$	$\frac{3}{2}B$
$[a_1b_2e^3]$	0	0	0	$\sqrt{27}B$	$6B$	$\sqrt{\frac{3}{4}}(3B+C)$	$\frac{1}{2}(3B+C)$	$\frac{3}{2}B$	$\sqrt{\frac{3}{4}}B$
$[b_1b_2e^3]$	0	0	0	$\sqrt{3}B$	0	$-\sqrt{\frac{3}{4}}B$	$\frac{3}{2}B$	$-\frac{1}{2}(B+C)$	$\sqrt{\frac{3}{4}}(B+C)$
$[b_1b_2e^3]$	0	0	$\sqrt{54}B$	0	$\sqrt{3}B$	$\frac{3}{2}B$	$\sqrt{\frac{3}{4}}B$	$\sqrt{\frac{3}{4}}(B+C)$	$\frac{1}{2}(B+C)$
...									

^2E	...	$[a_1^2b_1^2e]$	$[a_1^2b_2^2e]$	$[b_1^2b_2^2e]$	$[a_1b_1b_2^2e]$	$[a_1b_1b_2^2e]$	$[a_1b_1^2b_2e]$	$[a_1b_1^2b_2e]$	$[a_1^2b_1b_2e]$	$[a_1^2b_1b_2e]$
...										
$[a_1^2b_1^2e]$		$15B+10C+12K-$ $-12L+M$	C	$4B+C$	0	0	$\sqrt{\frac{3}{2}}B$	$-\sqrt{\frac{81}{2}}B$	$-\sqrt{\frac{9}{2}}B$	$-\sqrt{\frac{27}{2}}B$
$[a_1^2b_2^2e]$			$15B+10C+12K+$ $+12L+M$	$4B+C$	$\sqrt{\frac{75}{2}}B$	$-\sqrt{\frac{9}{2}}B$	0	0	$-\sqrt{18}B$	0
$[b_1^2b_2^2e]$				$45B+10C-$ $-7M$	$\sqrt{\frac{75}{2}}B$	$\sqrt{\frac{9}{2}}B$	$\sqrt{24}B$	$-\sqrt{18}B$	0	0
$[a_1b_1b_2^2e]$					$26B+9C+6K+$ $+6L-3M$	$\sqrt{3}B$	$3B$	0	$-\sqrt{12}B$	$3B$
$[a_1b_1b_2^2e]$						$22B+9C+6K+$ $+6L-3M$	$\sqrt{27}B$	0	$6B$	$\sqrt{3}B$
$[a_1b_1^2b_2e]$							$\frac{49}{2}B+9C+6K-$ $-6L-3M$	$-\sqrt{\frac{27}{4}}B$	$\sqrt{\frac{75}{4}}B$	$\frac{3}{2}B$
$[a_1b_1^2b_2e]$								$\frac{47}{2}B+9C+6K-$ $-6L-3M$	$\frac{3}{2}B$	$\sqrt{\frac{147}{4}}B$
$[a_1^2b_1b_2e]$									$\frac{39}{2}B+9C+12K+$ $+M$	$\sqrt{\frac{27}{4}}B$
$[a_1^2b_1b_2e]$										$\frac{33}{2}B+9C+12K+$ $+M$

(11c) (cont.)

$^1B_1$	$[a_1^2b_2e^2]$	$[b_1^2b_2e^2]$	$[a_1b_1b_2e^2]$
$[a_1^2b_2e^2]$	$18B+6C+6K+6L+4M$	$4B+C$	$-\sqrt{6}B$
$[b_1^2b_2e^2]$		$18B+6C-6K+6L-4M$	$\sqrt{6}B$
$[a_1b_1b_2e^2]$			$13B+5C$

(4)

$^1B_2$	$[a_1^2b_1e^2]$	$[b_1b_2^2e^2]$	$[a_1b_1b_2e^2]$
$[a_1^2b_1e^2]$	$18B+6C+6K-6L+4M$	$4B+C$	$\sqrt{6}B$
$[b_1b_2^2e^2]$		$18B+6C-6K+6L-4M$	$-\sqrt{6}B$
$[a_1b_1b_2e^2]$			$13B+5C$

(5)

^4E	$[a_1b_1e^3]$	$[a_1b_2e^3]$	$[b_1b_2e^3]$	$[a_1b_1b_2^2e]$	$[a_1b_1^2b_2e]$	$[a_1^2b_1b_2e]$
$[a_1b_1e^3]$	$16B+6C-6K+$ $+6L+3M$	0	$\sqrt{12}B$	$3B+C$	$-3B$	$\sqrt{3}B$
$[a_1b_2e^3]$		$16B+6C-6K+$ $+6L+3M$	$\sqrt{12}B$	$-3B$	$3B+C$	$\sqrt{3}B$
$[b_1b_2e^3]$			$12B+6C-$ $-12K-M$	$\sqrt{3}B$	$\sqrt{3}B$	$B+C$
$[a_1b_1b_2^2e]$				$16B+6C+6K+$ $+6L-3M$	0	$\sqrt{12}B$
$[a_1b_1^2b_2e]$					$16B+6C+6K-$ $-6L-3M$	$\sqrt{12}B$
$[a_1^2b_1b_2e]$						$12B+6C+$ $+12K+M$

(6)

The energy expressions (1)—(11) find their main uses in the interpretation [4] of the spectral properties of four-coordinate transition metal complexes.

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ТЕТРАГОНАЛЬНО ДЕФОРМИРОВАННЫЕ ТЕТРАЭДРИЧЕСКИЕ КОМПЛЕКСЫ ML_4. IV

Расщепление d^5-конфигураций в сильных полях лигандов D_{2d} симметрий

М. И. Бан

Используя приближение сильного поля, рассчитали энергетическое состояние электронов, происходящих из расщепления конфигураций создаваемых из d^5 электронных структур в лигандных полях D_{2d} (деформированные тетраэдрические) симметрии, в зависимости от параметров электростатических и лигандных полей, а также угла деформации.